Glass and Ceramics, Vol. 70, Nos. 7 – 8, November, 2013 (Russian Original, Nos. 7 – 8, July – August, 2013)

UDC 666.11.01:535.323

CHANGE IN THE CHARACTERISTICS OF NANOCOATINGS BY AGGRESSIVE MEDIA: EFFECT OF THE ETCHING SOLUTION

A. B. Atkarskaya[1]

Translated from *Steklo i Keramika*, No. 8, pp. 8 – 11, August, 2013.

The change induced in some parameters of a nanocoating by 0.1 N solutions of hydrochloric and nitric acids was studied. It was found that swelling is more intense in hydrochloric than in nitric acid. The intensity of the dissolution of a nanocoating in a 0.1 N solution of nitric acid is directly proportional and in hydrochloric acid inversely proportional to the etch time.

Key words: sol-gel technology, nanocoating, composite, index of refraction, thickness of nanocoating.

The present work continues investigations of the stability of sol-gel nanocoatings in aggressive liquid media [1].

The aim is to determine the changes in the index of refraction and thickness of composites with nanocoatings in 0.1 N solutions of hydrochloric and nitric acids.

Samples with the dimensions 50 × 50 × 4 mm were cut from a large-format composite consisting of float glass on which a nanofilm was deposited by the sol-gel technology. The samples were kept at room temperature in water solutions of hydrochloric or nitric acids with concentration 0.1 N. The interaction time varied from 1 to 180 min. The interaction occurred at room temperature.

The index of refraction n and thickness h of the films before (n_{ini}, h_{ini}) and after (n_e, h_e) etching and after post-etching firing ($n_{e.f}$, $h_{e.f}$) at 450°C were measured with a LÉF ZM 1 ellipsometer.

The interaction of the nanocoating with a liquid aggressive medium is comprised of two mutually opposite phenomena. The swelling due to the penetration of liquid into the pores of the xerogel of the nanocoating is accompanied by an increase of the thickness, while dissolution initiates the opposite process.

The change in the parameters of the coating as a result of the simultaneous action of swelling and dissolution can be estimated as

$$\Delta h_{s+d} = (h_e - h_{ini})/h_{ini};$$

$$\Delta n_{s+d} = (n_e - n_{ini})/n_{ini}.$$

[1] Novorossiisk Affiliate of the V. G. Shukhov Belgorod State Technological University, Novorossiisk, Russia (e-mail: atkarsk06@mail.ru).

The effect of dissolution can be followed according to the values of

$$\Delta h_d = (h_{ini} - h_{e.f})/h_{ini};$$

$$\Delta n_d = (n_{e.f} - n_{ini})/n_{ini}.$$

The effect of swelling rate on refractive index can be followed according to the values of

$$\Delta h_i = (h_e - h_{e.f})/h_{ini};$$

$$\Delta n_i = (n_{e.f} - n_e)/n_{ini}.$$

The computational results are presented in the figures.

The changes produced in the thickness h^{hca}, h^{na} and refractive index n^{hca}, n^{na} of nanocoatings by hydrochloric (‘hca’) and nitric (‘na’) acids in the course of swelling (Fig. 1*a*) and dissolution (Fig. 1*b*).

The change in the film thickness during swelling, determined according to the difference $h_e - h_{e.f}$, is maximum for interaction time 1 min and is practically the same (31 and 29%) for hydrochloric and nitric acid solutions. Subsequently, the swelling slows down to 11 – 20% in HCl and 0 – 15% in HNO_3.

In general, swelling is more intense in hydrochloric acid, which could be associated with the difference in the acid strength determined by the ionization constant, equal to 1×10^7 for hydrochloric and 43.6 for nitric acid [2].

The difference of the refractive indices ($n_{e.f} - n_e$) is not so large, reaching a maximum of 6 and 4% for HCl and HNO_3 acids, respectively, in 1 min and is in accord with the change in the thickness of nanocoatings during swelling.

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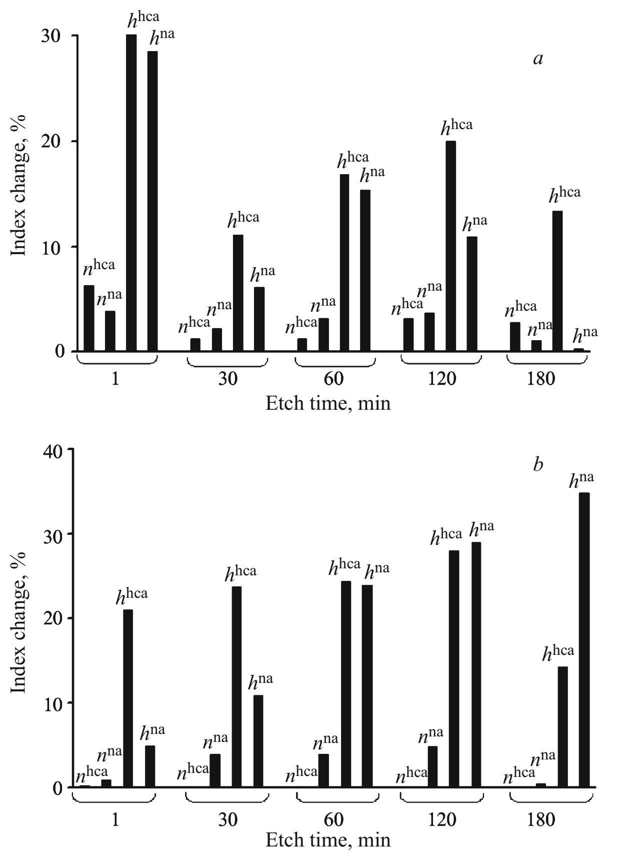

Fig. 1. Change in the index of refraction n and thickness h of nanocoatings as a result of the interaction of hydrochloric acid (hca) and nitric acid (na) at the swelling (a) and dissolution (b) stages.

The loss of coating thickness during dissolution in hydrochloric acid increases from 21 to 28% as etch time increases to 120 min and subsequently decreases to 14%.

In the case of interaction with HNO_3 coating dissolution intensifies in proportion to the etch time from 5 to 35%.

As a result of coating dissolution the refractive index of composites, independent of the nature of the etching agent and interaction time, is greater than the initial values. This difference does not exceed 0.2% for hydrochloric acid and is always greater for nitric acid, reaching 4.8%.

It is evident in Fig. 2 that under the action of the hydrochloric acid solution the intensity of the change in the refractive index and the thickness of nanocoatings at all stages of etching is inversely proportional to the interaction time. The trend lines are identical, but their slope angles are somewhat smaller for thickness changes. Such changes in the properties attest to some slowing of the swelling and dissolution in time.

If it is true that that the increase in the index of refraction after etching is associated with, among other things, washing out of the low-index oxides migrating from the substrate into the nanocoating, then the observed slowing is explained by the high rate of the interaction of these oxides with hydrochloric acid as compared with the solubility of the products of decomposition in water.

In contrast to the action of HCl, in 0.1 N nitric acid swelling slows to zero as the interaction time increases to 180 min, which is evidently associated with the dependence of the kinetics of swelling of the film material on the nature

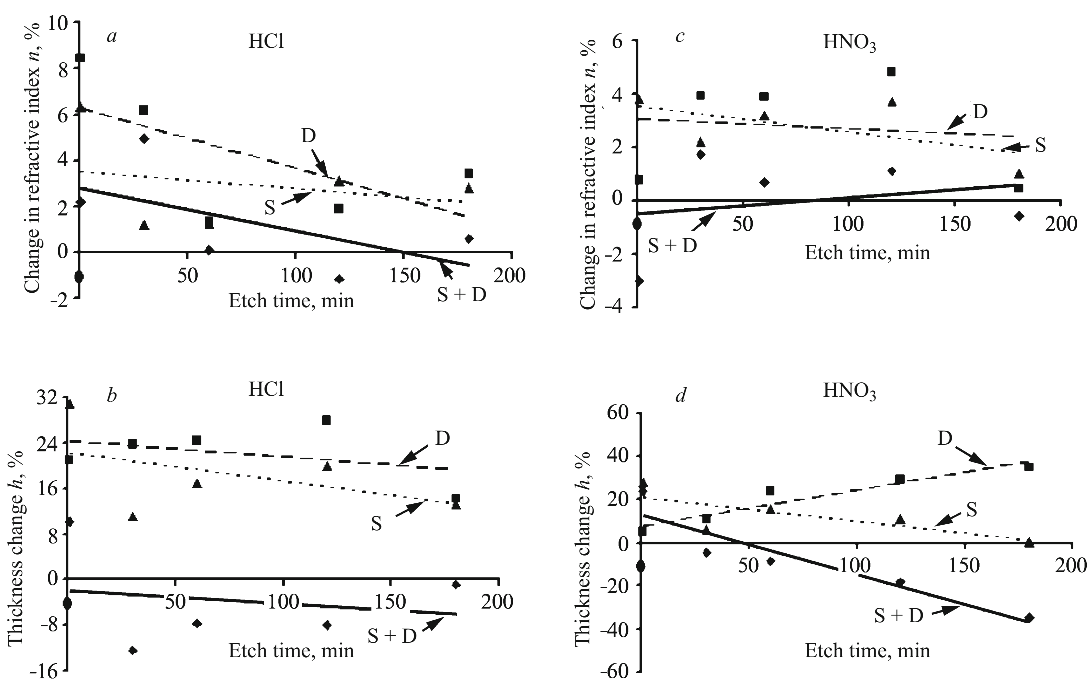

Fig. 2. Change in the refractive index (a, c) and thickness (b, e) of nanocoatings versus the etch time in hydrochloric acid (a, b) and nitric acid (c, d) solutions. The labels on the trend lines characterize the interaction stages: S) swelling, D) dissolution, S + D) combined effect of swelling and dissolution.

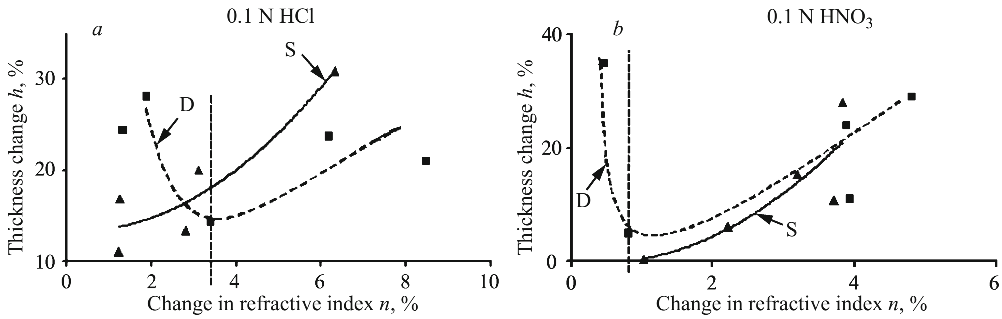

Fig. 3. Interrelationship of the changes in the refractive index n and thickness h of nanocoatings under the action of hydrochloric acid (a) and nitric acid (b) solutions at the swelling S and dissolution D stages.

of the acid. The intensity of the dissolution of nanocoatings is proportional to the etch time. It is possible that this effect can be explained better by the solubility in water of nitric acid products of interaction as compared with hydrochloric acid products.

For example, the solubility at 20°C, g/100 g H_2O is as follows [2]:

$NaCl$ – 35.9;

$NaNO_3$ – 82.9;

$CaCl_2$ – 74.5;

$Ca(NO_3)_2$ – 128.8.

Immediately after the nanocoating interacts with the acid solution, when the combined effect of swelling + dissolution can be followed according to the change in the parameters of interest, the indices Δh decrease with increasing etch time, and in the process the slope angle of the trend line for the process with hydrochloric acid is smaller, which could be associated with more active slowing due to the low solubility of the hydrochloric acid products of interaction.

The change Δn is inversely proportional to the interaction time of the nanocoating with the hydrochloric acid solution and directly proportional to the interaction with the HNO_3 solution, which could be associated with the dependence of the kinetics of dissolution and swelling of nanocoatings on the nature of the acid.

The interrelationship of the changes in the refractive index and thickness of nanocoatings at different stages of the interaction is demonstrated in Fig. 3. The decrease in the thickness due to dissolution reaches a minimum of 14 and 4%, which corresponds to the changes of 2 and 0.1%, respectively, in the index of refraction in hydrochloric and nitric acid processes. To the left and right of these points dissolution intensifies and Δh increases, accompanied by an increase on the right-hand and a decrease on the left-hand branches of the refractive index curves for the nanocoating. At the same time swelling intensifies on the right-hand branch, which probably intensifies the washing out of low-index oxides of the substrate that during deposition penetrate into the nanocoating layer, and as a result the refractive index increases.

On the left-hand branches of the plots the swelling and washing out of low-index oxides decrease and correspondingly Δn decreases.

The results of this work can be briefly summarized as follows.

- The swelling of a nanocoating is more intense in hydrochloric acid than in nitric acid, which could be associated with a difference in acid strength.
- The intensity of dissolution of a nanocoating in a 0.1 N solution of nitric acid is directly proportional and in hydrochloric acid inversely proportional to the etch time. This can be explained by the higher solubility in water of nitric acid products of interaction as compared with hydrochloric acid.

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